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Structural characterization and electrical conductivity of naphthalene doped polyblend films of polystyrene (PS) and polymethyl methacrylate (PMMA)

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Abstract : A thermally stimulated depolarization conductivity (TSDC) investigation in short circuit configuration have been carried out on physical blend of polystyrene (PS) and polymethyl methacrylate (PMMA) with composition 80 20 and naphthalene doped blend (PS PMMA). The films of undoped blend and naphthalene doped blend were prepared by isothermal evaporation technique Thermoelectrets of these films are formed at polarizing temperature 343 K and different polarizing field (*Ep*) 3, 5, 10,15 kV/cm. The depolarization conductivity recorded as a function of temperature and polarizing fields were characterized by two well defined peaks The first peak is obtained at 338 ± 5 K due to the low temperature β relaxation and second peak at 363 ± 5 K may be due to the higher temperature α relaxation The magnitude of peak conductivity increases linearly with the polarizing field.

Keyword : Thermally stimulated depolarizing conductivity, polymer blend, thermoelectrets

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1. Introduction

Polymers are capable of storing charge permanently when subjected to field temperature treatment. Such quasi-permanently charged dielectrics are then referred to as electrets [1]. The application of amorphous or semicrystalline polymer as electrets, however, requires the knowledge of conductivity of polymers, of their charge storage capability and of charge decay as a function of temperature. It has also been established that electret properties depend on the details of the structure and dynamical properties of the polymer, at both molecular and semimolecular levels [2].

Thermally stimulated discharge current (TSDC) of polymethly methacrylate (PMMA) films and sensitized PMMA with malachite green films were studied as a function of

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polarizing fields for different electrodes system. The effect of polarity reversal of the polarizing field on TSDC was also studied [3].

Patil *et al* [4] have studied thermally stimulated depolarization current in short circuit configuration of polyvinyl chloride (PVC), polymethyl methacrylate (PMMA) and their blends (PVC : PMMA) of different weight composition ratio as a function of polarizing field and polarizing temperature. Belsare and Deogaonkar [5] have reported the electrical conductivity of iodine doped polyblend film of polystyrene (PS) and polymethyl methacrylate (PMMA). Deshmukh *et al* [6] studied the electrical conduction in mixed polymer films; polyvinylchloride (PVC) and polymethyl methacrylate (PMMA) have been studied by finding the I-V characteristics at various temperature in the range of 323 K to 363 K. The results are presented in the form of I-V characteristic and analysis has been made in the light of Poole Frenket, Fowler-Nordheim, Schottky, Richardson and Arrehenius plots.

Thermally stimulated depolarization current investigation in short circuit configuration has been carried out on blends of an amorphous polymer polyphenylene oxide (PPO) and semicrystalline polymer polystyrene (PS). Different blend compositions were polarized at various temperatures ranging from 308 K to 383 K with different field. The polarization currents recorded as a function of temperature and field were characterized by two well defined peaks. The low temperature peak has been identified as the manifestation of the dipolar processes associated with the orientation of molecular dipoles attached to the phenyl groups. The high temperature peak is appearing a complex relaxation process associated with the motion of excess charges together with dipolar reorientation [7].

Recently, considerable amount of work has been reported on steady-state electrical conduction in insulating polymeric films. The work reported earlier emphasized on different interpretations for the observed results but it seems no ultimate view has yet been reached. The elucidation of the underlying charge injection and carrier migration process is vital to the future utility of these materials.

2. Experimental details

2.1. Sample preparation :

Polystyrene supplied by Polymer Chemical Industry, Mumbai, polymethyl methacrylate supplied by Dental Products of India, Mumbai and naphthalene by S G Sisco Pvt. Ltd., New Delhi, were used for the study. Thin films were prepared by isothermal evaporation technique [8], and it is best suited to the laboratory condition. The polymer blends were prepared by dissolving the two polymers in weight proportion 80 : 20 (PS : PMMA) in common solvent cyclohexanone (AR grade, supplied by E Merck India Ltd., Mumbai). Then it was kept at 323 K in temperature controlled muffle furnace for 12 h to obtain a homogenous solution. Then naphthalene was added to the homogenous

solution of polyblends in different weight percent (5%, 10%, 20%, 30%). Thin films were prepared by pouring the solution on a pool of mercury for perfect leveling so as to ensure uniform thickness. The whole system was allowed to evaporate at room temperature in dust free chamber and after complete evaporation the film was detached from the glass surface.

2.2. Thickness measurement :

The thickness of sample was measured by the compound microscope in conjunction with an occoulometer having a least count of 15.38 μm, similar to the method reported by Mehendru and Chand [9]. The thickness of all samples was kept constant and is of the order of 61.58 μm.

2.3. Electrode coating :

The electrode coating of the film of measured thickness was done by using the quick drying and highly conducting silver paste supplied by Eltecks Corporation, Bangalore. A mask of a circular aperture of 2.5 cm diameter was used while coating, to ensure uniformity in the size of the coated silver electrode.

2.4. Structural characterization :

For structural characterizartion the X-ray diffractograms of undoped polyblend and naphthalene doped polyblend films were obtained on XRD-PKL 1729 Phillips Bulk XRD (Pune University, Pune) and as shown in Figure 1. The X-ray diffractograms of all the samples were obtained for ensuring the nature of the film (amorphous or crystalline). The presence of naphthalene in PS : PMMA polyblend thin film was confirmed by IR spectra of the sample taken on FTIR-8400 spectrophotometer.

2.5. Measurement of thermally stimulated discharge conductivity :

2.5.1. Electret preparation :

Electroded sample was sandwiched between two brass electrodes of the sample holder. The metal polymer metal (M-P-M) system so formed was placed inside the furnace. The M-P-M system was heated at a nearly uniform rate upto polarizing temperature Tp = 343 K and was maintain at that constant temperature for half an hour. Different polarizing fields (Ep) 3 kV/cm, 5 kV/cm, 10 kV/cm, 15 kV/cm were applied using a stabilized d.c. voltage source for one hour keeping the field ON. The sample was slowly cooled to room temperature under continuing electric stress. Total time of polarization was adjusted to be 2.5 hours in each case. After polarization, the field was removed and the sample was short circuited for 20 minutes in order to remove stored charges if any. The electrets were prepared at different polarizing fields.

2.5.2. Thermally stimulated discharge current :

After the electret formation, the M-P-M assembly was placed in controlled temperature

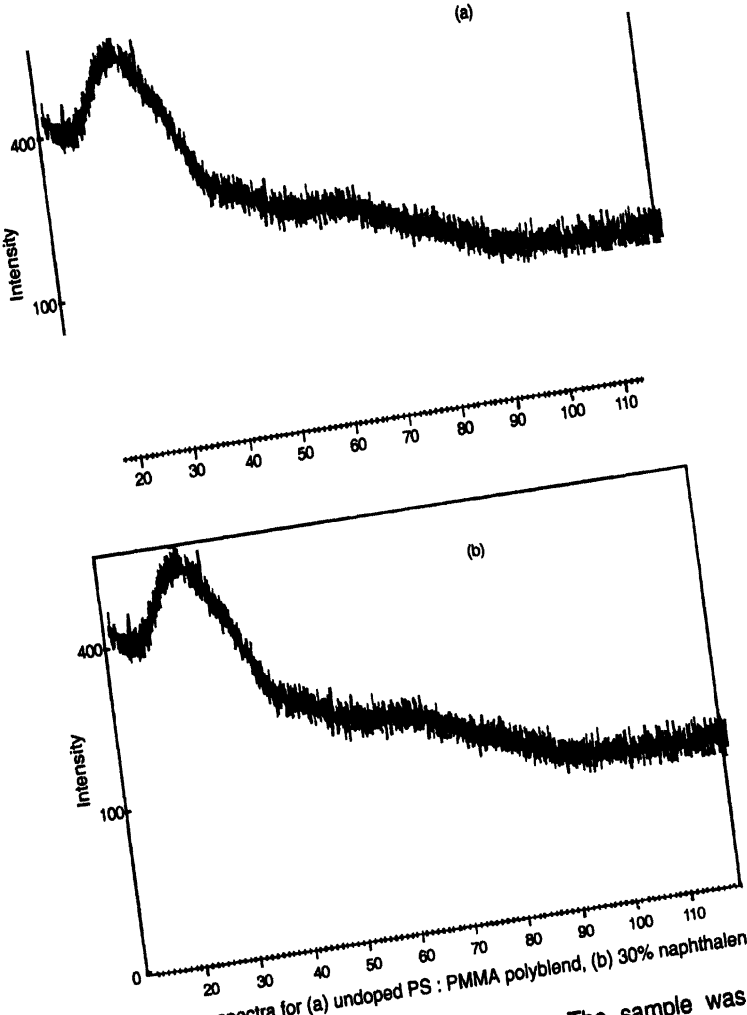

Figure 1. XRD diffraction spectra for (a) undoped PS : PMMA polyblend, (b) 30% naphthalene doped polyblend.

furnace supplied by Pushpa Scientific, Hyderabad. The sample was short circuited through a sensitive picoammeter (Model DPA III Scientific Equipment, Roorkee, having on accuracy of ±1 pA) for measurement of discharge current. The sample was thermally discharged at a uniform rate of 2 K/min from 313 K to 403 K.

3. Results and discussion

3.1. XRD analysis :

Figure 1 shows the diffraction pattern of undoped polyblend and 30% naphthalene doped polyblend. The absence of peak in X-ray spectra of undoped polyblend and naphthalene doped polyblend confirmed the amorphous nature [6]. Diffraction pattern of

remaining samples are similar and hence to avoid repetition, spectra are not given.

3.2. IR analysis :

The infrared spectra are much used for straight forward identification of specific functional group in the sample. The infrared spectra of undoped and naphthalene doped polyblend are observed in the range 500 cm^{-1} to 4000 cm^{-1}. Figure 2(a) shows the IR spectra of undoped PS : PMMA polyblend film. The IR spectra of PS : PMMA polyblend shows the aromatic C–H stretching, >C=C< stretching in presence of PS and

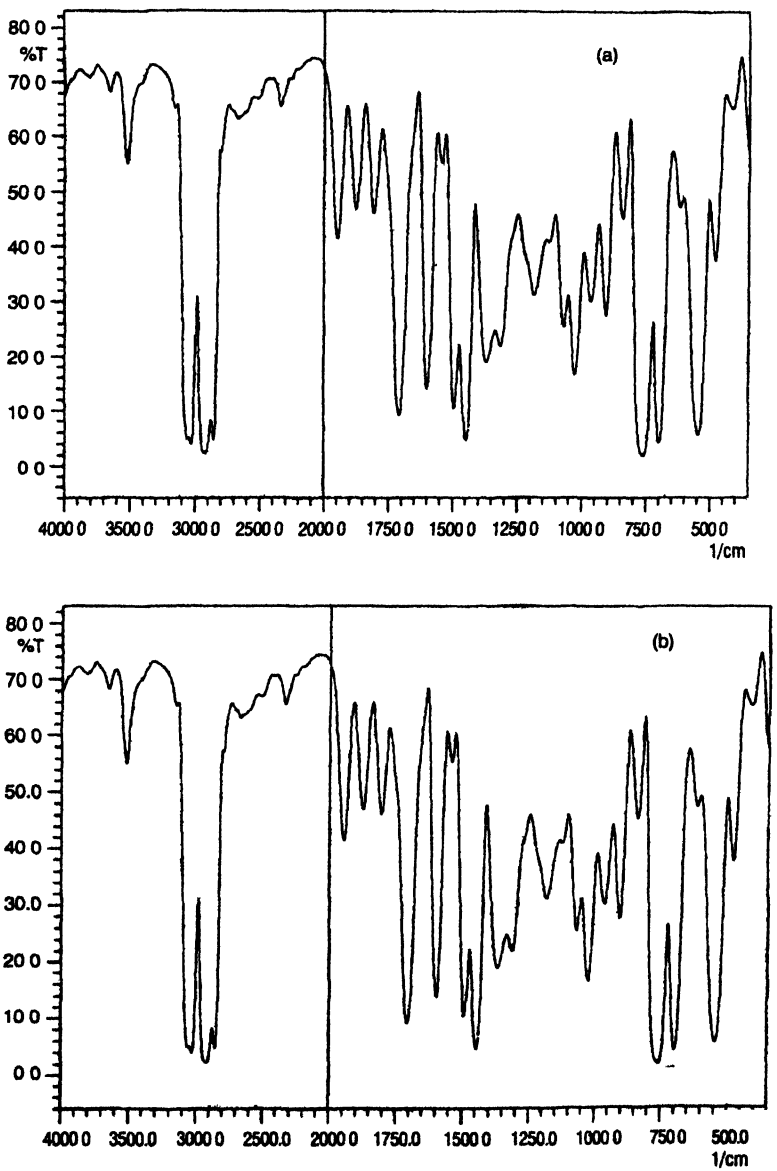

Figure 2. Infrared spectra of (a) undoped PS : PMMA polyblend, (b) 30% naphthalene doped polyblend.

>C=0 stretching (1735.80 cm^{-1}), C–O stretching (1244 cm^{-1}) in ester group in presence of PMMA. Figure 2(b) shows the IR spectra of 30% naphthalene doped polyblend. The IR spectra of naphthalene doped PS : PMMA polyblend are all most similar to that of undoped PS : PMMA polyblend.

3.3. Thermally stimulated discharge conductivity (TSDC) :

Typical TSDC thermograms for undoped PS : PMMA (80 : 20) polyblend and 30% naphthalene doped polyblend polarized at temperature 343 K with various polarizing fields 3 kV/cm, 5 kV/cm, 10 kV/cm, 15 kV/cm are shown in Figure 3 and Figure 4 respectively. The thermograms are characterized by a low and high temperature peaks. The first peak obtained is at 338 ± 5 K and it is due to the low temperature β relaxation and second peak at 363 ± 5 K may be due to the higher temperature α relaxation. The magnitude of peak conductivity increases linearly with the magnitude of polarizing field. It happens in polymers that the individual dipoles are randomly oriented. If an external d.c. electric field is applied, these dipoles tend to rotate under the action of this applied field finds, it difficult to bring about this rotation of dipoles and requires higher energy of activation.

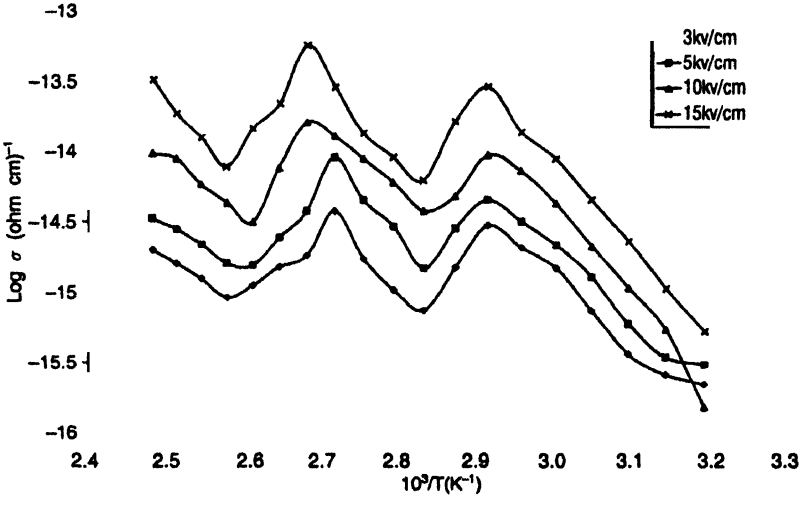

Figure 3. TSDC thermograms for undoped PS : PMMA polyblend with various polarizing fields 3, 5, 10 15 kV/cm.

The polarization in a polymer can arise from orientation of dipoles and trapping of charge carriers in different traps [10]. The dielectric relaxation processes occurring in PMMA are a high temperature α relaxation near its glass transition temperature between 363 K and 371 K and a β relaxation associated with the motion of carbonyl side group near 303 K. PS exhibits a high temperature, α-relaxation near 363 ± 5 K and low temperature β relaxation around 338 ± 5 K coupled to the motion of phenyl side group [11,12].

It is evident that the heights of the two peaks increase with increase in

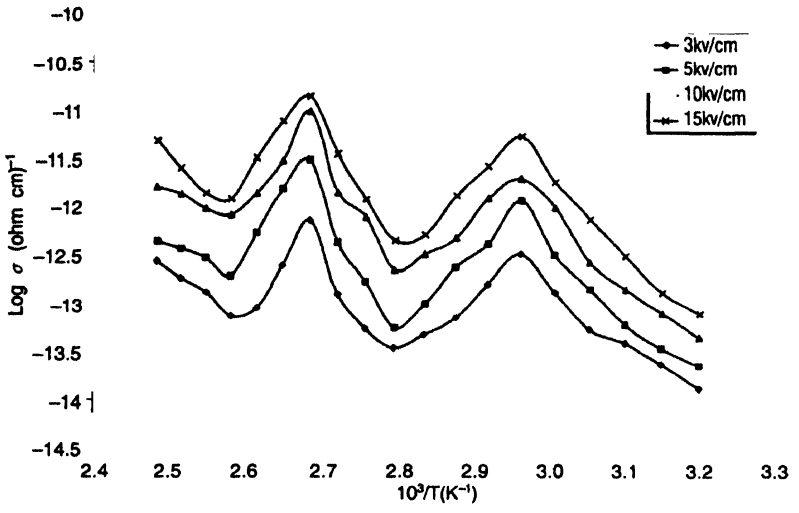

Figure 4. TSDC thermograms for 30% naphthalene doped PS : PMMA polyblend at various polarizing field 3, 5, 10, 15 kV/cm.

temperature. The position of the peak shifts to higher temperature side at higher polarizing field. This may be due to stronger polarization of the sample at higher fields, which in turn, requires higher temperature to release the charge carriers. At higher temperature, greater number of charge carriers are released from the relatively strongly polarized samples and therefore there is also the increase in magnitude of TSD conductivity with higher polarizing field.

Generally, polymer films consist of both crystalline and non crystalline (amorphous) regions. In the present study, all the samples, undoped PS : PMMA blend and naphthalene doped blend samples are amorphous in nature this is confirmed by X-RD as shown in Figures 1. Such polymers can exist in two states depending on temperature. At low temperature they are glassy hard materials while at higher temperature, they undergo transition to a rubber like state.

At glass transition temperature (*Tg*), gross molecular motion of the polymer chain accompanies the transition from the glassy to the rubbery state. The conductivity behavior of such films may be dominated by the properties of amorphous regions [13]. Presence of amorphous regions gives rise to localized states. Since there are many localized states, the release or excitation of the carriers in these states dominates the conduction process. The molecules of dopant enter either in the amorphous regions of the polymer or at the disordered regions like chain folds. If they are present in low concentration they will give rise to additional molecular sites for trapping of charge carriers. Such localized sites formed by dopant molecules can be defined in molecular terms using the different ionization potentials as an indication of trap depth.

Figure 5 shows TSDC thermograms of undoped polyblend and naphthalene doped (5%, 10%, 20%, 30%) polyblend at constant polarizing field 10 kV/cm. By keeping the

Increase in naphthalene percentage enhances both dipolar and induced dipole polarization on account of the formation charge transfer complex. The charge carriers gain higher mobility due to the addition of trapping sites created by the addition of naphthalene. Due to this they require less energy to get released. Decrease in activation energy is therefore, noticed on doping of naphthalene.

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